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WABASH - RDX MANUFACTURE: A LABORATORY EXAMINATION
OF THE AMMONIUM NITRATE PROCESS

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October 1975

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The optimized "AN" (ammonium nitrate) process for preparing RDX, developed some years ago at Wabash River Ordnance Works on a laboratory level, has been checked and verified. Items considered included yield and quality of RDX, recovery and recycle of excess ammonium nitrate, recovery of excess nitric acid, and its stabilization by controlled fume-off. The process is considered ready for study on a large scale		

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OBJECTIVE

The objective of the work described in this report was to check, on a laboratory scale, the optimized Wabash ammonium nitrate procedure for the manufacture of RDX prior to possible pilot and plant scale operations (see Ref 1).

INTRODUCTION

The Hale process for manufacturing RDX gives poor yields based on the hexamine and nitric acid used (117 g RDX per 100 g hexamine, or a 37% yield at one mole hexamine for two moles RDX). It was found, during World War II independently in England, Germany, and the USA, that the addition of ammonium nitrate in the Hale process greatly increased the yield of RDX to as much as 209 g per 100 g hexamine, a 68% yield. This approach was not developed further at the time, but was reviewed at the Wabash River Ordnance Works in the 1950's. They established the basis for a practical process by showing that the substantial excesses of ammonium nitrate and nitric acid used could be easily recovered and (in the case of the ammonium nitrate) recycled. No further development work was done at the time, however. Improvements in nitric acid technology during the 1960's led to renewal of interest in this type of process and cost studies of the AN process were made (Ref 2, 3). These showed that the AN process gave RDX at a significantly lower cost (12-14¢ per lb) than the Bachmann process now in use (17-20¢). It was therefore decided that the AN process merited further development, and that the first step should comprise checking the basic Wabash data, obtained on a 5 g hexamine level.

PROCEDURE

The optimum Wabash procedure (Ref 1) consists of dissolving 9.6 parts of dried ammonium nitrate in 17.2 parts of nitric acid (99.5% minimum). The addition of one part of hexamine is then made at 25°-50°C and the resulting reaction mixture is heated at 85°C for 30 minutes. Cooling, followed by drowning of the reaction mixture on ice, or recovery of nitric acid by vacuum distillation, and subsequent drowning of the residual cake, leads to yields of 63-65% based on two moles of RDX being derived from one mole of hexamine. A typical run using five grams of hexamine, 48 grams of ammonium nitrate, and 86 grams of nitric acid results in yields of RDX of 10.0 to 10.4 grams.

The procedure followed in this study was to dissolve in a flask equipped with a thermometer, stirrer, and reflux condenser with drying tube, 48.0 grams (0.6 mole) of oven dried (105°C) ammonium nitrate in 86.0 grams (1.36 moles) of nitric acid. This step was quite exothermic, and external cooling was employed to prevent the temperature from rising above 30°C. The use of "absolute" nitric acid, obtained by vacuum distillation from an appropriate mixture of 98% nitric acid and 30% fuming

sulfuric acid, resulted in slow solution of the ammonium nitrate; whereas solution of ammonium nitrate in 98% nitric acid was rapid. The resulting solutions in all cases were orange in color.

The ammonium nitrate-nitric acid solution is then cooled to about 23°C and five grams (0.035 mole) of hexamine were added in portions, with stirring, at 23°-28°C. (The initial additions of the hexamine dispelled the orange color and a small amount of gas evolution was observed.) After the addition of the hexamine, the reaction vessel was placed in a steam heated water bath at 85°C. This reaction temperature was maintained for 30 minutes during which time considerable fuming took place, and an orange color returned to the reaction mixture. Recovery of most of the excess nitric acid was now accomplished by carefully subjecting the mixture to vacuum distillation (15-20 mm Hg) and collecting the nitric acid distillate in a flask cooled by a dry ice-acetone bath. Generally, 50-65 grams of frozen nitric acid were collected. This acid, upon melting and warming to room temperature, underwent a vigorous, spontaneous fume-off resulting in gentle reflux, and the evolution of large quantities of brown oxides of nitrogen. This fume-off was apparently the result of the reaction between nitric acid and organic fragments from the hexamine, possibly formaldehyde. Analysis of this spent acid by titration with standard sodium hydroxide solution showed it to consist of about 92% nitric acid.

As the vacuum distillation of the reaction mixture progressed, a considerable amount of solid precipitated and a thick slurry formed which could not be poured from the reaction flask. It was "thinned" with ice-cold water and poured into additional water. The insoluble, crude RDX was collected on filter paper by suction, washed thoroughly with water to remove any residual nitric acid and ammonium nitrate, and then air dried.

Early nitrolyses did not incorporate recovery of excess nitric acid and the reaction mixture was simply drowned on crushed ice, the RDX was collected, washed with water, and dried.

Unreacted ammonium nitrate was recovered by evaporating the aqueous filtrate from the RDX filtration step and drying the residue at 105°C. This material generally had a tan color, presumably due to the presence of organic matter, and weighed about 40 grams. The use of this recovered ammonium nitrate in subsequent nitrolyses was not found to be detrimental to the yield of RDX.

RESULTS

Table 1 summarizes a group of nitrolyses using yellow nitric acid of about 98% concentration. The ammonium nitrate used in each nitrolysis was fresh material, and the reaction mixture was quenched on ice; the RDX so produced was white in color. It showed no impurities by NMR analysis. The reported melting points are uncorrected.

Table 2 tabulates the results of three nitrolyses using yellow 98% nitric acid and employing vacuum distillation to recover most of the unreacted nitric acid. Unreacted ammonium nitrate was recovered as previously described to be dried and used in later runs.

The effect of using recovered ammonium nitrate was examined in the series of nitrolyses listed in Table 3. The quantities of reactants in this series remained the same as in previous runs and the origin of the recovered ammonium nitrate used is indicated in the tabulation as the run numbers from which it was derived. Most of the unreacted nitric acid was recovered by vacuum distillation, allowed to fume off, and then discarded. It can be seen that the yield of RDX was not greatly affected, although the crude product was slightly off-white in color.

The use of freshly distilled "absolute" nitric acid was examined and the results are shown in Table 4. This acid was obtained by distilling under vacuum (15-20 mm Hg, 30°C) a mixture consisting of 201 ml of 98% yellow nitric acid and 47 ml of 30% fuming sulfuric acid. The nitric acid collected in this manner was practically colorless and was stored cold prior to use. Use of this nitric acid led to an increase in the yield of RDX as shown in Table 4. The origin of the ammonium nitrate used is indicated as in Table 3. Most of the unreacted nitric acid was recovered by vacuum distillation.

CONCLUSIONS

The optimized Wabash procedure for the manufacture of RDX has been investigated on the laboratory scale and found to be satisfactory. Ammonium nitrate can be recovered and used in subsequent nitrolyses without any adverse effects on the yield of RDX. The recovery of unreacted nitric acid is possible but the hazard of spontaneous fuming, particularly in large scale operation, must be kept in mind. Finally, the yield of crude RDX can run as high as 68%, provided that fresh vacuum distilled nitric acid is used in the nitrolysis.

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1. S. M. Overstreet, *RDX Manufacturing Process*, Report No. 27, Wabash River Ordnance Works, Liberty Powder Defense Corporation, 26 April 1957
2. J. A. Ruth, *Economic Evaluation of Candidate Processes for Manufacture of RDX*, Hercules Inc., 30 November 1972
3. R. W. Hutchinson, *Economic Review of Nitric Acid and Bachmann RDX Processes*, Explosives Division File Memorandum, 14 November 1973

Table 1

Nitrolyses using 98% nitric acid

Run #	Hexamine g	NH_4NO_3 g	HNO_3 g	RDX g	% yield	M.P. °C
265-33	5.00	48.0	86.0	9.58	60.4	200.5
265-34	5.00	48.0	86.0	9.50	60.0	201
265-35	5.00	48.0	86.0	9.72	61.3	200
265-36	5.00	48.0	86.0	9.58	60.4	200.5
265-37	5.00	48.0	86.0	9.70	61.3	200.5
265-39	5.00	48.0	86.0	9.54	60.2	200.5
265-38 ^a	3.95	48.0	86.0 ^a	0.08	0.6	200

^aRun No. 265-38 was an aborted run due most likely to the presence of excessive oxides of nitrogen in the nitric acid. This acid was obtained by distilling a mixture of 98% nitric and 30% fuming sulfuric acids at ambient pressure and turned out to be dark orange in color. After 3.95 grams of hexamine had been added, a vigorous fume-off occurred. Some of the reaction mixture was lost and a yield of only 0.08 gram of RDX was obtained.

Table 2

Nitrolyses employing nitric acid and ammonium nitrate recovery

Run No.	Hexamine g	NH_4NO_3 g	HNO_3 g	RDX g	% yield	MP °C	NH_4NO_3 recovered g	HNO_3 recovered g
265-42	5.00	48.0	86.0	9.64	60.8	201	39.0	55.8
265-43	5.00	48.0	86.0	9.42	59.4	201	40.5	58.3
265-44	5.00	48.0	86.0	9.55	60.2	201	<u>39.6</u>	52.5
							119.1 g total	

Table 3

Nitrolyses using recovered ammonium nitrate

Run No.	NH ₄ NO ₃ origin (run no.)	RDX g	% yield	M.P. °C	NH ₄ NO ₃ recovered g	HNO ₃ recovered g
265-45	265 - 42-4	9.64	60.8	201	39.5	65.9
265-46	265 - 42-4	9.60	60.6	201	35.6	52.1
265-47	265 - 42-4 +26 g fresh	9.50	59.9	201	40.3	55.3
265-48	265 - 45-7	9.45	59.6	200.5	38.6	61.2
265-49	265 - 45-7	9.53	60.1	201	39.6	62.6
265-50	265 - 48, 9	9.45	59.6	201	39.2	55.5

Table 4

Nitrolyses using absolute nitric acid

Run No.	NH_4NO_3 origin	RDX g	% yield	M.P. °C	NH_4NO_3 recovered g	HNO_3 recovered g
762-32	Fresh	10.75	67.8	201	39.9	56.2
762-54	Fresh	10.76	67.8	200.5	40.0	55.2
762-63	Fresh	10.67	67.3	200.5	40.1	59.8
762-53	39g 762-50 9g 762-49	10.55	66.5	200.5	39.6	53.6